(12) UK Patent Application (19) GB (11) 2 229 189 (13) A

(43) Date of A publication 19.09.1990

(21) Application No 9002992.7

(22) Date of filing 09.02.1990

(30) Priority data
(31) 8903300 (32) 14.02.1989 (33) GB

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(51) INT CL[5]
C09K 9/02, B42D 15/10, C09D 11/10 // B42D 223:00

(52) UK CL (Edition K)
C3V VAE
B6A AC52 ATC
U1S S1413 S2241 S2271 S2272

(56) Documents cited
GB 2214191 A GB 2195270 A GB 2192006 A
EP 0265323 A1 WO 89/05464 A1

(58) Field of search
UK CL (Edition J) B6A AK ATC, C3V VAE
INT CL[4] B42D, C09D, C09K
WPI, Claims (Dialog)

(54) Ink composition for security documents

(57) A durable security document (e.g. a banknote or credit card) comprises a photochromic dye substantially uniformly dispersed or dissolved within a translucent thermoset polymer matrix. An ink for printing on a suitable substrate comprises the dye in the matrix, a major proportion of a binder and minor amounts of one or more of driers, waxes, antioxidants and ultraviolet filters.

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INK COMPOSITION

This invention relates to photochromically-pigmented inks and to their use in security documents.

Security documents, by their very nature, need to incorporate a variety of different measures in order to defeat counterfeiting. Visual measures are designed to be seen with the naked eye. Machine-readable features are designed to be used with particular detectors and may not be viewable. Inks for security documents, and especially currency, must possess special qualities if they are to retain their properties for the life of the document, withstanding the rigours of handling and contamination.

GB-A-2195270 discloses photochromic inks for use in security documents, containing "fulgides" and "fulgimides". The photochromic dye compounds are normally invisible, but become visible on exposure to ultraviolet radiation. Such dyes have to be protected by an oxygen barrier layer, which considerably limits their utility, and requires an extra manufacturing step. In the absence of such a protective layer, the dye will function correctly only for a limited time; indeed, if applied directly as an unprotected ink, it will not be sufficiently durable for the normal demands on security documents, especially currency.

GB-A-2195270 indicates, further, that photochromic compounds may be incorporated into inks, as photochromic pigments obtained by incorporating such a compound into a finely-divided powder of a polymer such as pmma. The photochromic pigment is suspended in an ink varnish, and the viscosity of the ink may be adjusted by adding solvent.

GB-A-2214191 discloses photochromic prinking inks. In one method for their preparation, a low molecular

weight thermoplastic is melted with a photochromic dye. In a second method, the photochromic dye is microencapsulated. In a third method, the photochromic compound is included in an ink binder which is cured after printing.

WO-A-8905464 discloses a pigment which is a particulate photochromic material comprising a photochromic substance within a matrix of a polymerisate of a polyfunctional acrylate monomer. The material may be produced by subjecting the substance and the monomer to polymerisation, e.g. emulsion polymerisation. Glass and plastic composites having a photochromic response can thus be prepared.

WO-A-8802371 and US-A-4720547 disclose photochromic spiroindoline benzoxazine compounds which, on exposure to ultraviolet radiation, turn from colourless to coloured. The effect is reversible. Such compounds can be used in products such as goggles, glasses and windshields.

Wilson, Physics in Technology, Vol. 15 (1984) pages 232 - 238, describes the use of photochromic dyes for a variety of applications, including security. Wilson indicates that it could be possible to imbibe photochromic fulgides into finely powdered polymers which then can be included in the ink as a pigment. Wilson suggests this for letterpress and screen printing, but fails to explain exactly how this would be done.

Imbibition of a dye into a polymer means that the dye is meant to diffuse into the polymer through a mutual solvent which must then be evaporated. The selection of a suitable solvent can present difficulties. Common volatile solvents are often unsuitable. Less common, higher molecular weight and less volatile solvents, must then be selected. Some polymers, such as PVC, do not readily imbibe dyes. There is also a danger that any

solvent softening of the polymer would cause the particles to agglomerate.

The demands on printed security documents dictate that they must have sufficient durability that the document has a reasonable life. The requirements placed on banknotes are particularly stringent, because of the wide range of conditions which a banknote must undergo. For example, there must be adequate atmospheric oxidation-resistance, heat-, light- and humidity-resistance, resistance to mechanical damage such as folding and crumpling, resistance to soiling through handling, and resistance to inadvertent washing, laundering and solvent leaching. Durable light fastness is therefore important.

Photochromic compounds have very particular molecular structures. The photochromic properties are known to be readily degradable, under various conditions, which means that they lack the stability essential for banknote and similar uses. Imbibed photochromic dyes are relatively close to the plastic surface and therefore prone to degradation and leaching from the matrix, with attendant loss of photochromicity. The photochromic dyes near the surface are also prone to deterioration caused by free radicals.

Therefore, while imbibition is perhaps feasible on a small scale, it appears to be so impractical and expensive as to render it unworkable for the commercial exploitation of the materials which are described.

According to the present invention, a security document comprises, or is printed with an ink composition containing, as a pigment, a photochromic dye dispersed or dissolved within a translucent thermoset polymer matrix. A novel ink composition comprises such a pigment, a major proportion of a binder and minor amounts of one or more of driers, waxes, antioxidants and ultraviolet filters.

The polymeric matrix allows light to penetrate to a degree such that the photochromic effect is viewable or readable. The polymeric matrix may be tinted with dyes or finely-divided pigments, to change the perceived colour response. The dyes may be coloured or fluorescent.

The photochromic compound may be dissolved in the polymerised matrix or may be present as a fine particulate dispersion, the particle size of the dye being considerably smaller than the final photochromic pigment particle size.

In certain circumstances, the photochromic compound may be adsorbed on a surface such as an inorganic adsorbent such as clay. See GB-A-2104539.

Finely particulate additives may be included in small proportions, along with the photochromic dye, e.g. tinting pigments or metallic powders. More than one photochromic dye may be present in the matrix.

Other additives which do not affect the photochromic compound may also be included. While stabilisers to ultraviolet light and oxygen "sinks" may be included, it is generally undesirable to incorporate any compounds which are liable to be leached from the polymeric matrix and thus expose the photochromic dye to environmental attack.

For the purposes of this invention, the photochromic compound is preferably substantially evenly blended within the thermoset matrix and little is present solely at the surface of the pigment. It is preferred that there is an even distribution of dye within the pigment or a greater concentration towards the centre of the particle.

The photochromic dye is deeply interspersed, and so is trapped within the matrix. Preferably the matrix is a rigid cross-linked, cured polymer which provides good durability. Within a hard matrix, there is little

likelihood of the dye being chemically attacked, being leached out by solvent, or being attacked by free radicals. This enhances the durability of the photochromic effect which is particularly necessary for security printing purposes.

The term "thermoset" is adequately defined in WO-A-8905464, and suitable thermoset polymer matrix materials are defined therein. In particlar, any translucent polyment such as cross-linked polycarbonate, polyester, epoxide, polyurethane or, preferably, polyacrylate, may be used in this invention.

Photochromic dyes may also be incorporated into plastics as a dispersion or by an adhesive coating which may then be used in a security printed item. Examples of carrier polymers which may include the photochromic pigment are polyethylene, polyvinyl chloride, polyester and polycarbonate. The photochromic materials may be included, for example, in the adhesive coating of a protective plastic overlay film or in a banknote thread.

Suitable photochromic dyes are fulgides and fulgimides but are preferably spiroindoline benzoxazine compounds. Examples of photochromic dyes are given by Yoshida, Graphic Arts Japan Vol. 17 (1975-6) 52-56 and in WO-A-8905464, GB-A-2195270, GB-A-1464603, GB-A-2002572, GB-A-2146327, GB-A-2190379 and GB-A-2193005.

The pigments used in the invention may be prepared by condensation or addition polymerisation (emulsion polymerisation is a possible alternative), and cross-linking in the presence of the photochromic compound, to form a thermoset matrix. The compound then becomes well dispersed within the matrix. An example of such a pigment is Photosol 3972 supplied by PPG Industries Ltd.

Alternatively, the dye may be dissolved or dispersed in a solution of the polymer which may then be

spray-dried, to form the pigment. These and other methods are described in WO-A-8905464.

More preferably, a finely-divided photochromic pigment may be coated with the polymer to form a protective coating around the dye. The coating may be deposited by coating the particles with a solution of the polymer in a volatile solvent and then rapidly evaporating the solvent.

Alternatively, the photochromic dye may be incorporated into the matrix before polymerisation, or imbibed into particles of the polymer, to form core particles which are then coated with a translucent protective polymeric layer which may incorporate, say, colourants, fluorescers and/or further photochromic dye. This will provide durable photochromic particles.

The illumination source used to read a security document of the invention may emit in the visible and/or ultraviolet regions of the spectrum. It may be for example, a xenon flash source filtered to transmit ultraviolet light. Light having a wavelength of 300-400 nm, preferably 320-330 nm, is ofen used.

Preferably, the ink is an intaglio ink, but letterpress, screen and lithographic inks may also be used. In general, an ink composition of the invention comprises 1 to 50%, preferably 5 to 35%, by weight of the photochromic pigment (i.e. the particles dispersed in the matrix), and a major amount of a binder. For example, a suitable intaglio ink formulation consists of 20% by weight pigment and 78% binder, together with conventional additives such as driers and waxes. The formulations may be further stabilised by use of additives such as antioxidants and ultraviolet absorbers.

The pigment may have a particle size of between 0.1 and 20 µm, preferably 0.5 to 5 µm. The particle size for pigments used in lithographic inks is ideally less than 1

μm. For intaglio inks, the range is typically from 1 to 20 μm, preferably 1 to 10 μm, e.g. 1 to 5 μm.

The photochromic pigment used in the invention may be colourless or coloured, depending on its nature. It may change its visible absorbance after exposure to, say, either a strong flash, of milliseconds duration, from a xenon flash unit, or to a uv fluorescent tube for, say, 3-10 seconds. The photochromic effect lasts for some seconds, but gradually fades as the dye returns to the ground state.

The colour change is, for example, from colourless to blue, or from colourless to red. The pigment may have an initial cream appearance, and the colour changes may be from cream to blue or red.

Examples of security documents which may include the photochromically-pigmented ink are banknotes, currency, share certificates, bonds, passports, stamps, driving licences, permits, tickets, plastic cards, credit cards, charge cards, cash withdrawal cards, cheque cards, travellers' cheques, bank cheques, remote access control cards, and also visas. Photochromic ink printing may also be used on signature strips, for example for plastic financial cards. Alternatively, the photochromic pigments may be confined within a polymeric environment such as being encapsulated by polymer or extruded with a polymer. In such instances the photochromic pigments of this invention are then contained within the security document. Preferably they are printed onto the document.

The following Examples 1 to 4 illustrate the invention. All parts and percentages are by weight, unless otherwise specified.

Example 1

20% of a colourless-to-blue photochromic ink pigment (Photosol 3972, a spiroindoline derivative within a

thermoset matrix derived from a polyfunctional acrylate, supplied by PPG Industries, average particle size 2 μm), is blended with 79% binder (mixture of phenolic modified rosin and urethane-modified alkyds diluted with high boiling-point aliphatic hydrocarbon solvents), and 1% driers and other additives. The Photosol pigment consists of photochromic dye incorporated by polymerising the polymeric matrix of the pigment in the presence of the dye, thus forming a thermoset pigment for use in the compositions of the invention.

The ingredients were blended in a triple-roll ink mill, to obtain an intaglio ink. The ink was used on an intaglio proofing press, to print rag paper which bears lithographic security printing. The resulting banknote bore a colourless intaglio ink image. After exposure to high intensity xenon flash light, filtered to transmit ultra-violet light the intaglio print turned blue. Under microscopic examination, it was possible to discern that it was the intaglio ink which had changed colour. The blue ink was readily detectable as having been printed by intaglio, on microscopic examination, because of the characteristic raised pattern. The banknote exhibited durable photochromic properties.

Example 2

The procedure of Example 1 was repeated, except that a colourless-to-red pigment was employed. Again a durable photochromic response was obtained from the printed banknote.

Example 3

An offset lithographic ink was blended from the following (using a colourless-to-blue photochromic pigment supplied by PPG Industries under their Photosol brand name, average particle size 2 μm):

Photochromic pigment prepared by thermosetting the acrylate polymer in the presence of photochromic dye	20.0%
Phenolic modified rosin	23.5%
Drying oil	30.5%
Alkyd resin	15.6%
High boiling-point aliphatic hydrocarbon	3.4%
Wax	5.0%
Driers	1.0%
Anti-oxidant	1.0%

The ink was printed on to travellers' cheque paper having other security markings. The ink was colourless but exhibited a blue colour on illumination to ultraviolet from a filtered xenon flash source and exhibited a high level of durability.

Example 4

A PVC credit card substrate was security-printed with various lithographic inks, one of which contained a PPG Photosol photochromic pigment which is colourless but turns light blue on exposure to UV light of wavelengths 300-400 nm.

The substrate was covered with a thin PVC film which was then heat-laminated to the substrate, in order to make the card of tamperproof, integral construction.

A signature strip, intaglio printed with colourless-to-blue photochromic pigment, was then adhered to the front of the card.

On exposure to ultraviolet light from a filtered xenon flash gun, both photochromic inks changed colour and the credit card exhibited durable photochromic properties.

Example 5 (comparative)

The formulation of Example 1 was compared with a similar formulation lacking the photochromic pigment but

including 10% of the a photochromic dye obtained from PPG Industries as Type 0272: it was a spiroindoline derivative.

The materials were subjected to durability tests to establish the extent to which they would withstand exposure to light, humidity and various solvents. They were rated on a scale of 0 to 5, where 0 represents complete loss of photochromism and 5 complete retention, assessed visually. All the solvent tests were of short duration, approximately 30 minutes.

	Ex. 5	Ex. 1
Light fastness (40 hrs simulated daylight)	0	3
Humidity (60% RH, 30°C)	5	5
Ethyl acetate	0	2
Industrial methylated spirits	0	3
Petrol	0	5
Petroleum ether	0	5
Toluene	0	5
n-Octanol	1	5
Artificial sebum	0	5
Oxitol (Cellosolve)	0	4

It will be seen from the results that the ink composition according to the invention exhibited very significantly better photochromic responses under a range of widely different and stringent test conditions.

CLAIMS

1. A security document which comprises, as a pigment, a photochromic dye substantially uniformly dispersed or dissolved within a translucent thermoset polymer matrix.

2. A security document according to claim 1, wherein the matrix comprises a cross-linked polymer.

3. A security document according to claim 2, wherein the pigment has been obtained by condensation or addition polymerisation and cross-linking in the presence of the photochromic dye.

4. A security document according to claim 1, wherein the pigment has been obtained by spray-drying a solution or dispersion of the dye in the polymer.

5. A security document according to any preceding claim, which is printed with an ink composition containing the pigment.

6. A security document according to claim 3, which comprises a major proportion of a binder and minor amounts of one or more of driers, waxes, antioxidants and ultraviolet filters.

7. A security document according to claim 5 or claim 6, obtained by intaglio printing, wherein the ink composition is an intaglio ink formulation.

8. A security document according to any preceding claim, which is a banknote.

9. A security document according to claim 1, substantially as described in any of Examples 1 to 4.

10. An ink composition comprising a pigment, a major proportion of a binder and minor amounts of one or more of driers, waxes, antioxidants and ultraviolet filters, wherein the pigment is as defined in any of claims 1 to 4.

11. An ink composition according to claim 10, which comprises 1 to 50% by weight of the pigment.

12. An ink composition according to claim 10, which comprises 5 to 35% by weight of the pigment.

13. An ink composition according to claim 10, substantially as described in any of Examples 1 to 4.

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